

Corrosion Inhibitors for Use in New Concrete Construction



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**Corrosion Inhibitors for Use in
New Concrete Construction**

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Abstract:	This report presents a literature review of corrosion inhibitors and the findings of an experimental program examining the effectiveness of calcium nitrate and stannous chloride on corrosion protection. The experiments were conducted on steel samples submerged in oxygenated lime water containing calcium chloride. Corrosion measurements included visual inspection, half-cell potential, AC impedance, polarization resistance, and Tafel plot. Under the test conditions, calcium nitrite appeared to be a promising corrosion inhibitor. The nitrate/chloride ion threshold level for corrosion was between 0.07 and 0.09. Stannous chloride was found to be ineffective for corrosion protection in the range of dosage considered.
Key words:	corrosion inhibitors, corrosion of reinforcing steel, calcium nitrate, stannous chloride, electrochemical corrosion measurements
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1. INTRODUCTION

The ingress of chloride ions into reinforced concrete highway structures may result from run-off from bridge decks and splash from passing traffic. When sufficient chloride ions come into contact with the reinforcing steel, corrosion of steel occurs if oxygen and moisture are present.

Some admixtures are available and marketed as corrosion inhibiting admixtures. However, there are conflicting opinions on the effectiveness of these corrosion inhibitors.

A two-phase study on currently available corrosion inhibitors was initiated by the Ministry of Transportation and Communications (MTC). The purpose of this study is to determine the effectiveness of corrosion inhibitors for use in new concrete construction.

This report describes the findings from Phase I of this study and presents recommendations for Phase II.

In Phase I of the study, a literature survey was performed to collect background information on various corrosion inhibitors and methods used for inhibitor evaluation. From this information, the corrosion inhibitors having promising inhibiting properties and techniques suitable for inhibitor evaluation were identified. An experimental program was then carried out to examine the effectiveness of these corrosion inhibitors on protection of steel in oxygenated lime water containing various concentrations of calcium chloride. The objective of this test program was to examine the corrosion inhibiting mechanism and inhibitor/chloride corrosion threshold levels for the corrosion inhibitors under study.

Section 2 of this report describes the background of corrosion inhibitors and evaluation techniques. Sections 3 and 4 describe the experimental program and test results for the selected corrosion inhibitors, and Section 5 contains a recommendation for Phase II of the study.

2. CORROSION INHIBITOR

2.1 General

An ideal corrosion inhibitor is a chemical compound, which, when added in adequate amounts to concrete, can prevent corrosion of embedded steel and has no adverse effect on the properties of concrete.

Corrosion inhibitors can be divided into three types (1-4): anodic, cathodic, and mixed corrosion inhibitors.

Anodic corrosion inhibitors suppress the reaction at the anode by oxidising ferrous ions to form an insoluble film of hydrated ferric oxide adhering tightly to the anodic area. The inhibitor dosage required depends upon chloride concentration in the concrete. To be effective, an anodic corrosion inhibitor must be present in high concentration. When insufficient inhibitor is added, corrosion may become intensely localized and pitting corrosion can occur.

Anodic corrosion inhibitors include organic compounds, such as sodium benzoate, and inorganic salts, such as calcium and sodium nitrite, sodium and potassium chromate, stannous chloride, and sodium salts of silicate and phosphate.

Cathodic corrosion inhibitors retard the cathodic reaction by precipitating on the cathodic area to restrict diffusion of reducible species, such as oxygen, and to increase electrical resistivity of the system. The reactive products of cathodic corrosion inhibitors do not bond to the metal as tightly as those of anodic corrosion inhibitors and hence cathodic corrosion inhibitors may be less effective than anodic corrosion inhibitors. However, unlike anodic corrosion inhibitors, insufficient addition of most identified cathodic corrosion inhibitors is not likely to promote pitting corrosion.

Cathodic corrosion inhibitors include organic compounds, such as the aminoethanol group and aniline and its chlor-, alkyl-, and nitro- substituted forms; and inorganic salts which are strong bases, such as sodium hydroxide, sodium and calcium carbonate.

Mixed corrosion inhibitors influence both the anodic and cathodic processes. The molecules of mixed corrosion inhibitors may have more than one proton- and electron- acceptor orienting group attached (e.g. NH_2 and SH). An example of the mixed corrosion inhibitors is aminobenzenethiol.

For practical applications, the following guidelines can be used for evaluating the effectiveness of a corrosion inhibitor (4).

1. Degree of solubility
2. Compatibility with aqueous cement phase
3. Ratio of inhibition offered to the amount of inhibitor required
4. Rate of consumption of the inhibitor
5. Effect on setting time, strength, and durability of concrete

An effective inhibitor should be soluble in mixing water so that sufficient quantity of the inhibitor can be present at the corroding areas. However, the inhibitor should not be too soluble such that it readily leaches out of the concrete and hence loses its effectiveness.

The inhibitor must be compatible with the aqueous cement phase to develop its full potential for corrosion protection.

The amount of inhibitor required for effective inhibition increases with chloride ion content. If the ratio of inhibition offered to the amount of inhibitor required is low, the concentration of inhibitor would have to be very high. This may have adverse effect on the properties of concrete.

In order to provide prolonged protection for steel embedded in concrete, the rate of consumption of inhibitor should be low.

The side effects of inhibitor, if any, on time of set, strength, and durability of concrete should be fully examined. For example, it is known that alkalis (oxides of sodium and potassium) may react with some types of aggregates, and the products of the reaction cause disintegration of concrete.

2.2 Previous Work

Previous studies (5-24) have mainly focused on anodic corrosion inhibitors, especially calcium nitrite, sodium nitrite, stannous chloride, sodium benzoate, and some sodium and potassium salts. Some measurement methods were employed to evaluate the effectiveness of corrosion inhibitor. The measurement methods and major findings of these studies are described below.

2.2.1 Test Method

Test specimens used in these previous studies were:

1. Small steel specimens submerged in a saturated lime water containing different amounts of inhibitors and chloride
2. Reinforced mortar and concrete blocks containing inhibitors and either admixed with chloride or exposed to chloride environments
3. Large reinforced slabs containing inhibitors and either admixed with chloride or exposed to chloride environments

The methods for studying the effectiveness of corrosion inhibitors included:

1. Anodic polarization
2. Polarization resistance
3. Direct measurement of macrocell current
4. Half-cell potential measurement
5. Visual inspection

Three different methods of anodic polarization were used (5-14,16,17). In the first method, a constant current (or potential) was applied to steel specimens and the corresponding changes in potential (or current) were recorded with time. The effectiveness of an inhibitor was determined by examining the shape of the potential-time plot. Fig. 1 shows a typical potential-time plot.

Curves A, B and C in Fig. 1 represent three different inhibition processes. Curve A shows that the test specimen is passivated. The passivity is indicated by a rapid increase in potential at low current densities and the potential rises continuously and rapidly to the oxygen evolution range. Curve B shows that a test specimen is passivated initially (indicated by the rising portion of the curve) but the passivated film is destroyed and corrosion proceeds (indicated by a decrease in potential). Curve C shows that no passivity is achieved (indicated by a slow rise in potential). Thus, if a corrosion inhibitor exhibits substantial inhibitory property, the corresponding anodic polarization curve will be similar to Curve A.

In the second method, a range of currents (or potentials) was applied to test specimens and the induced potentials (or currents) were measured. The effect of an inhibitor on corrosion protection was determined by examining the shape of potential-current density plot, and the interpretation of the curve was similar to that in the first method.

While the first and second methods were performed on steel specimens in aerated lime water, mortars, or concretes (5-14), the third method was conducted mostly on steel specimens in deaerated lime water (16,17). In this method, a range of potentials was applied at a slow scan rate (about 0.2 mV/s) to test specimens and the corresponding currents were recorded. The polarization scan was then performed in the reverse direction. The inhibitory behavior of an inhibitor was evaluated qualitatively by examining the shape of potential-log current plot. Fig. 2 shows a typical potential-log plot.

In Fig. 2, E_n is the nucleation potential (the potential at which a pit is first observed). Higher E_n values indicate that longer time is needed to initiate pitting at a given scan rate. E_p is the pitting potential (the potential above which pitting can occur). When E_p is more positive than the corrosion potential of steel in concrete, pitting corrosion is not likely to occur. Hence, an inhibitor that raises E_p above -100 mV SCE will likely protect steel from chloride-induced corrosion. Curve A in Fig. 2 indicates the corrosion susceptibility of a test specimen is significantly reduced compared to a specimen behaving as in Curve B.

Measurement time for all three anodic polarization methods usually was 30 minutes or more. The applied currents were typically in a range of $10 \mu\text{A}/\text{cm}^2$ and potential shifts were more than 500 mV SCE. A new steel specimen had to be used for each test to obtain reliable results because of change in steel surface condition resulted from the large applied currents and potentials.

The polarization resistance technique (25) was used to estimate the corrosion rate of steel in mortar and concrete blocks (12-14,19). To obtain the corrosion rate of a steel sample, a set of small values of potentials (typically less than 20 mV CSE) is applied to the steel to shift the steel potential from its open-circuit potential. The slope of the applied potential and induced current plot, referred to as polarization resistance, is then substituted in the following equation:

$$I_o = \frac{1}{2.3 R_p} \left(\frac{\beta_a \beta_c}{\beta_a + \beta_c} \right) \quad [1]$$

where I_o is corrosion current, R_p is polarization resistance, and β_a and β_c are anodic and cathodic Tafel constants.

Equation 1 is valid only for a corroding system in which the corrosion process is controlled by activation energy. The values of β_a and β_c vary with different corroding systems. Assumed values of β_a and β_c were used in the previous studies.

In the FHWA study (18), macrocell corrosion currents between rebars embedded in chloride-contaminated and chloride-free concrete were examined. The rebars were electrically coupled and the macrocell currents were estimated from the measured voltage drops across resistors incorporated in the circuit.

Half-cell potential measurements were performed on steel bars embedded in mortars and concretes (10-15,19,22,23). This method indicates the probability of corrosion of a rebar based upon its electrical potential with respect to a reference electrode. Copper-copper sulfate electrode (CSE) and saturated calomel electrode (SCE) are commonly used as the reference electrodes. According to ASTM C876 (26), there is greater than 90 % probability that corrosion occurs when the steel potential is more negative than -350 mV CSE, but there is greater than 90 % probability that corrosion does not occur when the steel potential is less negative than -200 mV CSE. The corrosion activity is uncertain when the steel potential is between -200 mV and -350 mV CSE.

Visual inspection was used to examine corrosion of steel removed from mortars and concretes (10-15,19-22,24). Gravimetric mass loss was also determined in some cases (12,19). These methods are useful in evaluating the long-term effectiveness of corrosion inhibitor.

2.2.2 Calcium Nitrite

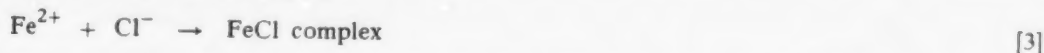
Among various anodic corrosion inhibitors, calcium nitrite has been studied most extensively (10-18). The roles of chloride and nitrite ions in the anodic reactions are probably as follows (10).

Under normal conditions, the reaction occurring at the surface of steel embedded in concrete is:



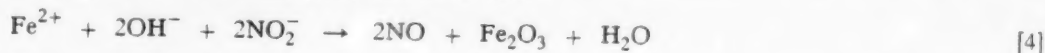
The ferrous hydroxide ($\text{Fe}(\text{OH})_2$) in Equation 2 subsequently converts to ferric oxide (Fe_2O_3), which adheres tightly to the steel surface.

In the presence of chloride ions, the ferrous ions in Equation 2 combine with chloride ions to form FeCl complex:



The ferrous ions are then released from the FeCl complex and converted to ferrous hydroxide at some distance away from the steel surface. Upon further oxidation, the ferrous hydroxide becomes rust.

When nitrite ions are present, the ferrous ions in Equation 2 react with nitrite ions to form gaseous nitrite oxide (NO) and ferric oxide:



Here, again, the ferric oxide is bonded to the steel surface and passivation is achieved.

Equations 3 and 4 show two opposing effects - chloride ions induce corrosion whereas nitrite ions inhibit corrosion. Hence, the chloride ions and nitrite ions compete with each other to react with ferrous ions in the anodic reactions. The total ferrous ion consumption is the combination of Equations 2, 3, and 4 and the reaction rate is unknown.

Rosenberg et al (10-14) showed that an addition of 1 to 3 % calcium nitrite substantially reduced corrosion of steel in mortar blocks containing admixed sodium chloride up to 3 % by mass of cement. Test results of half-cell potential measurements and visual inspections from large slabs also revealed that calcium nitrite considerably improved corrosion resistance of embedded steel. The authors indicated that corrosion protection offered by calcium nitrite might be more effective in high-strength concrete. Polarization resistance and anodic polarization with a constant applied current were used in the experiments.

Berke and Stark (16,17) showed that calcium nitrite improved significantly the corrosion resistance of steel in aerated and deaerated saturated lime water over a range of nitrite-chloride ratios (0.13 to 1.3). The tests were performed using anodic polarization with reverse scan.

Virmani et al (18) stated that an addition of calcium nitrite, at a ratio of nitrite to chloride ion of 0.8 or less, could provide more than an order of magnitude reduction in macrocell corrosion rate of rebars embedded in slabs. The tests were carried out using visual inspection and direct measurement of macrocell corrosion current.

Rosenberg et al (10) found that calcium nitrite, which acted as an accelerator, decreased setting time of concrete. Compressive strength of concrete increased with increase in calcium nitrite content over a dosage ranging from 2 to 5 % by mass of cement. The rate of increase in strength was more noticeable at low dosage.

Hope and Ip (27) found that additions of calcium nitrite of 0.5 % and 1 % by mass of cementitious materials in cement paste containing silica fume increased compressive strength of the paste. Test results from a preliminary study showed that electrical resistivities of the pastes containing 0.5 % and 1 % admixed calcium nitrite were comparable to that of the paste without calcium nitrite.

Virmani et al (18) indicated that electrical resistivity of concrete containing 2.75 % calcium nitrite by mass of cement was slightly lower than that of concrete without calcium nitrite.

According to these studies, calcium nitrite shows promising inhibitory properties. It can offer substantial corrosion protection to steel when an adequate amount is added. Electrical resistivity seems not to be a major factor influencing corrosion protection offered by calcium nitrite in the range of additions considered.

There is little information regarding nitrite/chloride corrosion threshold level and long-term effectiveness of calcium nitrite on corrosion protection in the literature.

2.2.3 Sodium Nitrite

Effects of sodium nitrite on corrosion of steel and strengths of mortar and concrete have been studied (5-9,19,22).

Gouda and Monfore (5) showed that an addition of 1 to 2 % sodium nitrite by mass of cement reduced considerably the corrosion susceptibility of steel embedded in concrete containing 2 % admixed calcium chloride. When 0.5 % sodium nitrite was used, steel samples were passivated initially but became active afterwards. The authors cautioned that sodium salt might be undesirable for use with aggregates which are known to be reactive with alkalis. The tests were performed using two anodic polarization methods (constant applied current and variable applied current).

Gouda and Halaka (6-8) showed that an addition of 1 to 2 % sodium nitrite by mass of cement effectively suppressed the corrosion of steel embedded in concrete containing 2 % admixed sodium chloride. Compared to other sodium and potassium salts, such as sodium chromate, sodium phosphate, sodium benzoate, sodium silicate, and potassium chromate, sodium nitrite required the lowest dosage to achieve a similar level of protection. The tests were conducted using anodic polarization with a constant applied current.

Gonzalez et al (19) found that an addition of 3 % sodium nitrite by mass of cement reduced considerably corrosion of steel embedded in carbonated mortar. The tests were performed using polarization resistance and half-cell potential measurement.

Chen et al (20) found that corrosion of rebars embedded in concrete containing 2 % admixed sodium nitrite by mass of cement was half that of rebars embedded in concrete without sodium nitrite. The tests were carried out by visual inspection of rebars after concrete slabs were exposed to seawater for 10 years.

Craig and Wood (9) showed that, while sodium nitrite offered substantial corrosion protection of steel, it caused a decrease in both tensile and compressive strengths of mortar. The corrosion tests were performed using anodic polarization with a constant applied current.

Treadaway and Russell (22) also concluded that sodium nitrite provided effective corrosion protection of embedded steel but it caused a decrease in concrete strength.

From these test results, corrosion protection offered by sodium nitrite is similar to that of calcium nitrite. This is probably because only nitrite ions are involved in the inhibition process. Sodium nitrite, however, may cause a decrease in strength of concrete and increases the risk of alkali-aggregate reaction for some susceptible aggregates. It may also be more susceptible to leaching and efflorescence than calcium nitrite (4).

2.2.4 Stannous Chloride

Corrosion resistance of stannous chloride and the effect of stannous chloride on strengths of mortar and concrete have been investigated (21,22).

Arber and Vivian (21) found that an addition of stannous chloride (up to 5 % by mass of cement) effectively suppressed corrosion of steel specimens embedded in mortar containing admixed calcium chloride (up to 4 % by mass of cement). The mortar blocks were steam-cured and corrosion of steel was examined visually after the blocks were broken. Stannous chloride increased tensile strength of mortar and acted comparably to calcium chloride in accelerating

strength development. A similar result for concrete containing stannous chloride was reported by Treadaway and Russell (22).

From these test results, it appears that stannous chloride, like calcium nitrite, shows promising inhibitory properties and has a beneficial effect on strength development of concrete.

2.2.5 Sodium Benzoate

Different findings on the inhibitory property of sodium benzoate have been reported (5,6,8,9,22,24).

Lewis et al (24) stated that sodium benzoate might have more persistent inhibitory effect than calcium nitrite.

Gouda et al (5,6,8) found that, compared with sodium nitrite, the dosage of sodium benzoate required to achieve a similar protection level in concrete containing 2 % admixed chloride was about six times higher.

Craig and Wood (9) indicated that sodium benzoate did not display passivity in mortar containing 2 % admixed calcium chloride and it caused a decrease in both tensile and compressive strengths of mortar. The strength decreased more markedly with higher dosages of sodium benzoate. A decrease in strength of concrete containing sodium benzoate has also been reported (22).

Based upon these test results, the effectiveness of corrosion protection offered by sodium benzoate is not clear. Sodium benzoate, similar to sodium nitrite, would be expected to cause a decrease in concrete strength.

2.2.6 Other Inorganic Salts

Some sodium and potassium salts (sodium chromate, sodium phosphate, sodium silicate, and potassium chromate) have also been investigated (5,6,8,9).

Gouda et al (5,6,8) found that these salts generally required higher concentrations to achieve a comparable protection level when compared to sodium nitrite.

Craig and Wood (9) indicated that potassium chromate, like sodium benzoate, provided no passivity for steel in mortar with 2 % admixed calcium chloride and it caused a decrease in compressive strength of mortar.

Based on test results of sodium nitrite and sodium benzoate, all of the above sodium salts would likely cause a decrease in strength of concrete and increase the danger of alkali-aggregate reaction for some types of aggregates. Therefore, these inhibitors appear to be less promising.

2.2.7 General Discussion

Among all the anodic corrosion inhibitors reported in the foregoing studies, calcium nitrite and stannous chloride seem to be most promising and further investigations of these is warranted.

There is little information about optimum dosage rates for calcium nitrite and stannous chloride and long-term effects of these corrosion inhibitors on corrosion protection of steel in

concrete. The optimum dosage rates can be estimated if inhibitor/chloride corrosion threshold levels for the two inhibitors are known.

Visual inspection and electrochemical methods may be used to monitor small steel samples in lime water containing corrosion inhibitors and chloride. These types of measurements can be performed quickly and provide information about inhibiting mechanism and inhibitor/chloride threshold level.

The anodic polarization methods used in the previous studies give useful information on the effectiveness of corrosion inhibitor. The change in steel surface condition due to the large applied potentials or currents is of concern and a new steel sample must be used for each test when these methods are used.

The polarization resistance technique can estimate corrosion rate of steel in an electrolyte. This method minimizes the disturbance of the test sample since only small potential shifts are applied to the test system. In addition, the measurement time of polarization resistance is the fastest among various electrochemical methods (typically 3 minutes or less). However, difficulties arise when determining the Tafel constants (necessary for conversion of polarization resistance to corrosion rate) and applying this technique in complex electrochemical systems (28).

The Tafel constants in the polarization resistance equation may be obtained from the linear portions of a Tafel plot, which is a plot of applied potential vs the logarithm of the resulting current. Corrosion rate can also be estimated directly from this plot. The potential shift in such a plot is typically 300 mV CSE. Again, because of the large magnitudes of applied potentials or currents, the condition of the steel surface would likely be changed. Therefore, a new steel sample must be used for each test when a Tafel plot is performed.

The AC impedance method (28-31) provides information on inhibitor performance and passive layer characteristics of steel. In this method, an electrochemical cell is represented by an equivalent electrical circuit. Electrode capacitance and charge-transfer kinetics of the cell are obtained graphically from impedance diagrams, such as Nyquist and Bode plots.

The excitation signal in AC impedance is a small AC signal (typically 10 mV or less) and does not disturb test system significantly. Therefore, the same steel sample can be monitored continuously to examine changes in passivity of steel corresponding to changes in inhibitor and chloride concentrations. The major disadvantage of this technique has been its complicated and time-consuming data acquisition and analysis. However, the acquisition and analysis of data are greatly facilitated using automated measurement systems which have recently become available.

3. TEST PROGRAM

3.1 Overview

This test program examined the inhibiting mechanism and inhibitor/chloride corrosion threshold levels for calcium nitrite and stannous chloride under a simulated concrete environment.

Test specimens were small steel samples submerged in oxygenated lime water containing different amounts of inhibitor and chloride. Corrosion on the steel surfaces was examined visually and electrochemically. The electrochemical measurements included AC impedance, polarization resistance, and Tafel plot.

3.2 Corrosion Inhibitors and Initiator

Two corrosion inhibitors, calcium nitrite powder and stannous chloride, were examined. The calcium nitrite powder was a commercial corrosion inhibitor. It was a fine white powder and contained 90 % calcium nitrite ($\text{Ca}(\text{NO}_2)_2$). The stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) was laboratory grade, fine, yellowish white crystals.

Both sodium chloride and calcium chloride have previously been used to initiate corrosion. Calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was used as corrosion initiator in this study. It was a laboratory grade, fine-granulated, white powder.

3.3 Test Cell

The test cell consisted of a 1-litre reaction kettle to contain various test solutions, a working electrode (steel sample), a platinum counter electrode, a calomel reference electrode, and a gas inlet through which oxygen was introduced to the test solutions. The arrangement of the test cell was similar to that described in ASTM G5-78 (32). Fig. 3 shows a schematic diagram of the test cell.

The electrodes and gas inlet were inserted into the reaction kettle using electrode holders (see Fig. 3). The steel sample was machined from 19 mm diameter Grade 400 reinforcing steel. Each specimen was 12.7 mm in length and 9.5 mm in diameter and was drilled, tapped, and mounted to an electrode holder. Prior to testing, each steel sample was cleaned with paper towel, polished with 600-grit SiC paper, and rinsed with distilled water. The active surface area of the steel sample was 4.5 cm^2 .

The counter electrode was a circular mesh type with a wire extension at one end. It was 30 mm in length and 15 mm in diameter and was mounted to an electrode holder at the wire extension.

The reference electrode was connected with a salt bridge filled with saturated lime water. The salt bridge extended to about 1 cm from the surface of steel sample.

The test solutions were saturated lime water with different concentrations of calcium chloride and corrosion inhibitor (calcium nitrite powder or stannous chloride). The lime water was prepared from calcium hydroxide powder and distilled water. Precautions were taken to prevent formation of calcium carbonate, which results from the reaction between lime and carbon dioxide in the air. The lime water was filtered into the reaction kettle, and calcium chloride and corrosion inhibitor were then added to the filtered lime water. The solutions were stirred continuously during testing.

3.4 Electrochemical Measurements

The electrochemical measurement equipment consisted of an EG&G PARC Model 273 potentiostat, an EG&G PARC Model 5208 lock-in analyzer, and a Zenith 158 microcomputer. Both the potentiostat and lock-in analyzer were remotely controlled by the computer via a National Instrument PC-2A IEEE interface.

Two EG&G PARC software programs, M378 and M342, were used to perform AC impedance, polarization resistance, and Tafel plot measurements.

In the AC impedance method, the system provided two measurement techniques: Lock-in Amplifier (LIA) and Fast Fourier Transform (FFT). With the LIA technique, the potentiostat applied a series of single sine waves to the test cell at frequencies ranging from 100 kHz to 5

Hz, and the lock-in analyzer measured the phase and amplitude characteristics of each of the waveforms.

With the FFT technique, the potentiostat digitally generated and mixed 20 potential sine waves, each with different frequency ranging from 10 Hz to 0.1 mHz. The potentiostat applied the resulting waveform to the test cell. The test system responded to this potential waveform with a complex current waveform which provided impedance information for each of the 20 discrete frequencies. The response was subsequently decoded into its 20 frequency components by the M378 software. The advantage of FFT technique is its fast measurement time at low frequencies compared to that of the LIA technique.

The M378 software had an option which allowed users to run multiple experiments in sequence. With this option, it was possible to run up to 5 LIA and/or FFT experiments, which together covered a wide frequency range with adequate data density. In this test program, a total of 4 experiments: 2 LIA and 2 FFT, was used for each measurement. The LIA experiments were performed over frequencies ranging from 100 kHz to 5 kHz, and the FFT experiments, from 10 Hz to 10 mHz. Total measurement time for these experiments was 40 minutes. The magnitude of applied AC signal was 10 mV.

For DC measurements, the system provide current interrupt IR compensation to compensate for the ohmic drop in the test cell and a low pass filter to subdue high frequency noise.

With the polarization resistance technique a short potential scan over a range of ± 20 mV SCE with respect to the open-circuit potential of the steel sample was performed. The scan rate was 0.2 mV/s and measurement time was 3 minutes. The M342 software calculated the corrosion current of the steel sample using Equation 1 described in Section 2.2.1 with specified values for β_a and β_c . In this test program, the values for β_a and β_c were obtained from Tafel plot when both polarization resistance and Tafel plot were conducted.

In Tafel plot measurement a potential scan over a range of ± 150 mV SCE with respect to the open-circuit potential of steel sample was performed. The scan rate was 0.2 mV/s and measurement time was 25 minutes. Corrosion rate, β_a , and β_c were calculated by the M342 software using a statistical curve fitting technique.

3.5 Test Procedure

Initially, it was decided that tests were to be conducted on steel samples in both aerated (oxygenated) and deaerated (nitrogenated) lime water. Test results from a preliminary study indicated that there was little corrosion on steel in deaerated lime water containing calcium chloride. Consequently, tests conducted in the main program were focused only on steel samples in oxygenated lime water, which was thought to be a more realistic model simulating the physical conditions in concrete.

A total of 3 test series were performed in the main program. Test series 1 and 3 were used mainly to examine the inhibiting mechanism of calcium nitrite. Test series 2 was used to examine the inhibiting mechanism and inhibitor/chloride corrosion threshold levels for calcium nitrite and stannous chloride.

Test Series 1: 1 % calcium chloride by mass of lime water was added initially to an oxygenated lime water. After a two-day conditioning period, 0.1 % calcium nitrite powder by mass of lime water was added in the solution. The concentration of calcium nitrite powder was increased with increments of 0.1 % to a maximum of 0.3 %. The conditioning period between each nitrite addition was 5 days.

Visual inspections and half-cell potential, AC impedance, polarization resistance, and Tafel plot measurements were conducted at each concentration level of chloride and nitrite and the measurements were taken at the end of each conditioning period. Two new steel samples were tested at each chloride/nitrite concentration level and a new solution was used for each steel sample.

The above test procedure was repeated for stannous chloride.

Test Series 2: 0.1 % calcium nitrite powder was added to an oxygenated lime water initially. After a 5-day conditioning period, 0.5 % calcium chloride was added to the solution. The concentration of calcium chloride increased with increments of 0.5 % to a maximum of 2.0 %. The conditioning period between each chloride addition was 2 days.

Visual inspections, half-cell potential, and AC impedance were performed at each concentration level of chloride and nitrite. Polarization resistance and Tafel plot tests were conducted only on steel in lime water containing 0.1 % calcium nitrite powder and 2 % calcium chloride. All the measurements were taken at the end of each conditioning period. The same steel sample was used throughout the tests. A total of 3 steel samples were investigated and a new solution was used for each steel sample.

The above test procedure was repeated for stannous chloride.

Test Series 3: A sample of the solution containing 1 % calcium chloride and 0.3 % calcium nitrite powder from test series 1 was retained for chloride and nitrite ion content analysis. The remainder of the solution was mixed with 0.1 % fine iron filings (about 40 mesh) by mass of lime water in order to accelerate the consumption of nitrite ions in the solution.

Three months after the addition of iron filings, two solution samples, one without iron filings and one with iron filings, were analyzed in the Department of Chemistry at Queen's for chloride and nitrite ion contents.

Six months after the addition of iron filings, corrosion measurements were conducted on two new steel samples in the solution containing iron filings using visual inspection, AC impedance, polarization resistance, and Tafel plot.

4. RESULTS AND DISCUSSION

4.1 Calcium Nitrite

4.1.1 Solubility

Calcium nitrite powder dissolved in lime water easily. It dissolved completely after mixing with the lime water for about a minute.

4.1.2 Inhibiting Property

Test Series 1: There was no corrosion on the steel surfaces after the steel samples were placed in oxygenated lime water. Electrical potentials of steel varied from -120 mV SCE to -150 mV SCE, indicating low probability of corrosion.

After the addition of 1 % calcium chloride, a few small rust spots were formed on the steel surfaces. Steel potentials became much more negative and were between -480 mV SCE and -520 mV SCE, showing high probability of corrosion.

Impedance diagrams indicated that the steel samples were under active corrosion. Fig. 4 shows a typical Nyquist plot. The semi-circle in the figure shows that the steel was corroding and the corrosion process was activation controlled (i.e. corrosion rate depended on the charge-transfer energy between the steel sample and solution). The charge-transfer resistance, which was equal to the chord length of semi-circle, was about 2 kohms. Note that the diffusion rate of oxygen was not a major factor in this corrosion process since the lime solution was saturated with oxygen.

Corrosion currents calculated from polarization resistance and Tafel plot were between $1.5 \mu\text{A}/\text{cm}^2$ and $3.0 \mu\text{A}/\text{cm}^2$.

After the addition of 0.1 % calcium nitrite powder, the steel surfaces were covered by a thin silvery-white coating, which adhered tightly to the steel surfaces. This coating appeared to be the protective ferric oxide film described in Section 2.2.2. Steel potentials decreased considerably and varied from -110 mV SCE to -200 mV SCE, indicating low probability of corrosion.

The passive film formation was also indicated in the impedance diagrams. Fig. 5 shows a representative Nyquist plot. The plot was dominated by a large incomplete semi-circle, showing that a passive film was developed on the steel surface. The passive film resistance, R_f , given by the chord length of semi-circle, was estimated to be 100 kohms.

Corrosion currents calculated from polarization resistance and Tafel plot were between $0.10 \mu\text{A}/\text{cm}^2$ and $0.40 \mu\text{A}/\text{cm}^2$, about one tenth of those for steel in lime water containing 1 % calcium chloride.

When the concentration of calcium nitrite powder was increased to 0.2 % and 0.3 %, the oxide coatings on the steel surfaces were more visible. Steel potentials decreased further and varied from +10 mV SCE to -50 mV SCE. R_f in the Nyquist plots increased to between 150 and 300 kohms. Corrosion currents calculated from polarization resistance and Tafel plot were negligible.

These test results indicated that reinforcing steel could be repassivated by calcium nitrite after corrosion had been initiated by calcium chloride. Under the given test conditions, an addition of 0.1 % calcium nitrite powder substantially suppressed the corrosion of steel in lime water containing 1 % calcium chloride. The steel samples were repassivated when the concentration of calcium nitrite powder reached 0.2 % or more. The ferrous ions appeared to react with nitrite ions to form a protective ferric oxide rather than combine with chloride ions to form iron-chloride complex.

Test Series 2: After the addition of 0.1 % calcium nitrite powder, similar to that in test series 1, a thin silvery-white film was formed on the steel surfaces and no rust spots were seen. Steel potentials varied from -10 mV SCE to -40 mV SCE, showing low probability of corrosion. Again, the formation of a passive film was indicated by the impedance diagrams. The Nyquist plots were comparable to that in Fig. 5, with an average R_f of 150 kohms.

After the addition of 0.5 % and 1 % calcium chloride, visual examination indicated that there was little change on the surfaces of steel. Steel potentials were in a range from -50 mV SCE to -160 mV SCE. R_f in the impedance diagrams, however, decreased gradually with increasing in chloride content.

When the concentration of calcium chloride was increased to 2 %, a few small rust spots developed on the steel surfaces and the color of some parts of steel surfaces changed from silvery-white to a darker color. Steel potentials increased significantly and were between -380 mV SCE and -410 mV SCE, indicating high probability of corrosion.

Fig. 6 shows a typical Nyquist plot for the steel samples. Although the shape of the curve was not well defined, it appeared that the curve consisted of two semi-circles. The semi-circle at the left represented the charge-transfer corrosion process, and the semi-circle at the right represented the passive film formation. In this case, the passive film seems to have been broken down by the chloride ions.

Corrosion currents calculated from polarization resistance and Tafel plot were between $0.9 \mu\text{A}/\text{cm}^2$ and $1.7 \mu\text{A}/\text{cm}^2$.

The passive oxide films on the surfaces of steel appeared to be destroyed and the steel samples were corroding when the concentration of calcium chloride in the solution was between 1.5 % and 2 %. In terms of the ratio of calcium nitrite powder to calcium chloride, the corrosion threshold level was probably between 0.05 and 0.07. Since the calcium nitrite powder contained 90 % calcium nitrite, the corrosion threshold level, in terms of the ratio of nitrite to chloride ions, was between 0.07 and 0.09.

Test Series 3: Chemical analysis on the two 3-month old solution samples was unable to reveal the chloride and nitrite ion contents in this solution due to the masking effect of the large ionic concentrations present.

The typical oxide coatings previously observed on passivated steel specimens were not visible on the surfaces of steel in the 6-month solution sample. A few small rust spots developed on the steel surfaces. Steel potentials varied from -380 mV SCE and -420 mV SCE, indicating high probability of corrosion.

Fig. 7 shows a Nyquist plot for a steel sample in the 6-month solution sample. The plot was comparable to that for the steel in lime water containing 0.1 % and 2 % calcium chloride (Fig. 6). R_t and R_f in this plot were about twice those in Fig. 6.

Corrosion currents calculated from polarization resistance and Tafel plot were between $0.4 \mu\text{A}/\text{cm}^2$ and $1.2 \mu\text{A}/\text{cm}^2$.

The effectiveness of calcium nitrite on corrosion protection was significantly decreased in the presence of iron filings. This could be because the actual concentration of nitrite ions in the solution was perhaps reduced as a result of consumption of nitrite ions by iron filings. Iron filings react with nitrite ions to form ferric oxide and nitrite oxide according to Equation 4 in Section 2.2.2. But this could not be substantiated by test data since the concentrations of nitrite and chloride ion in the two solution samples could not be obtained from the chemical analysis.

4.1.3 Summary

The calcium nitrite powder used in this study dissolved in lime water easily and could be mixed effectively with fresh concrete.

When the calcium nitrite powder was added to lime water prior to the addition of calcium chloride, the corrosion threshold level, in terms of the ratio of nitrite to chloride ions, was between 0.07 and 0.09.

Further experiments should be carried out to examine the effectiveness of calcium nitrite on corrosion protection of steel in concrete. These tests would be expected to provide useful information about the actual inhibiting properties of calcium nitrite on steel in concrete and long-term effectiveness of calcium nitrite on corrosion protection.

4.2 Stannous Chloride

4.2.1 Solubility

Stannous chloride did not dissolve completely in lime water. Small white particles were formed after stannous chloride was mixed with the lime water. These particles were dispersed throughout the solution when the solution was stirred continuously but precipitated at the bottom when the solution was at rest.

4.2.2 Inhibiting Property

Test Series 1: When 0.1 % stannous chloride was added in lime water containing 1 % calcium chloride, a few small rust spots were formed on the steel surfaces. Potentials of steel samples varied from -450 mV SCE to -480 mV SCE and were comparable to those of steel in lime water containing 1 % calcium chloride.

Impedance diagrams showed that the steel samples were corroding. Fig. 8 shows a typical Nyquist plot. The plot was comparable to that for steel in lime water containing 1 % calcium nitrite and 2 % calcium chloride (Fig. 6). R_i and R_f in this figure were about half those in Fig. 6.

Corrosion currents calculated from polarization resistance and Tafel plot were between $1.2 \mu\text{A}/\text{cm}^2$ and $2.6 \mu\text{A}/\text{cm}^2$.

There was no significant change in corrosion activity of steel samples when the concentration of stannous chloride was increased to 0.2 % and 0.3 %.

Test Series 2: When 0.1 % stannous chloride was added to lime water, a white coating was formed which adhered loosely on the surfaces of steel samples. No rust spots were seen on the steel surfaces. Steel potentials were between -160 mV SCE and -190 mV SCE, indicating low probability of corrosion.

The Nyquist plots were similar to those for steel in lime water containing 0.1 % calcium nitrite powder, suggesting that a passive film was formed on the steel surfaces.

After the addition of 0.5 % calcium chloride, a few small rust spots were developed on the steel surfaces. Steel potentials increased considerably and were between -460 mV SCE and -470 mV SCE, showing high probability of corrosion. Nyquist plots and corrosion currents from polarization resistance and Tafel plot were similar to those for steel in lime water containing 1 % calcium chloride and 0.1 % stannous chloride (Fig. 8).

4.2.3 Summary

Stannous chloride did not dissolve well in lime water; consequently, the solubility of this admixture in fresh concrete is a cause of concern.

Also, stannous chloride could not effectively protect steel against corrosion with the dosage used in this test program.

The foregoing test results showed that stannous chloride did not appear to be a good corrosion inhibitor.

5. RECOMMENDATION

Based on the test results from this Phase I study, calcium nitrite appears to be a promising corrosion inhibitor. Further study should be carried out to examine the effectiveness of calcium nitrite on corrosion protection of steel in actual concrete specimens. A recommended study for phase II is shown in the Appendix.

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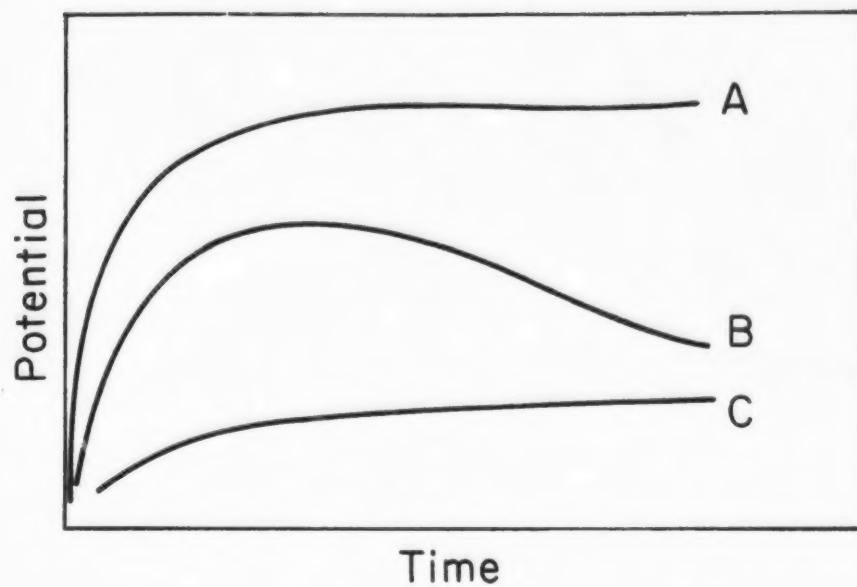


Fig. 1. Anodic polarization with constant applied current: Curve A - complete passivation; Curve B - partial passivation; Curve C - active corrosion

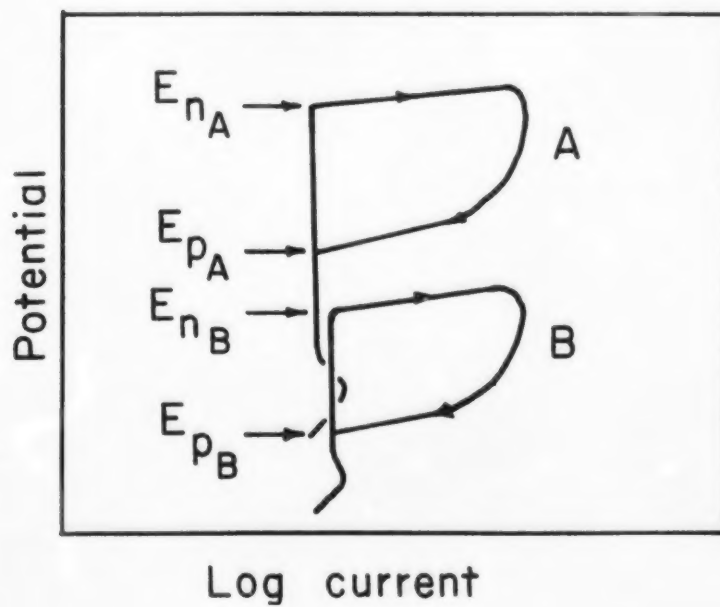


Fig. 2. Anodic polarization with reverse scan: Curve A - low corrosion; Curve B - high corrosion (arrows on Curves A and B indicate scan direction)

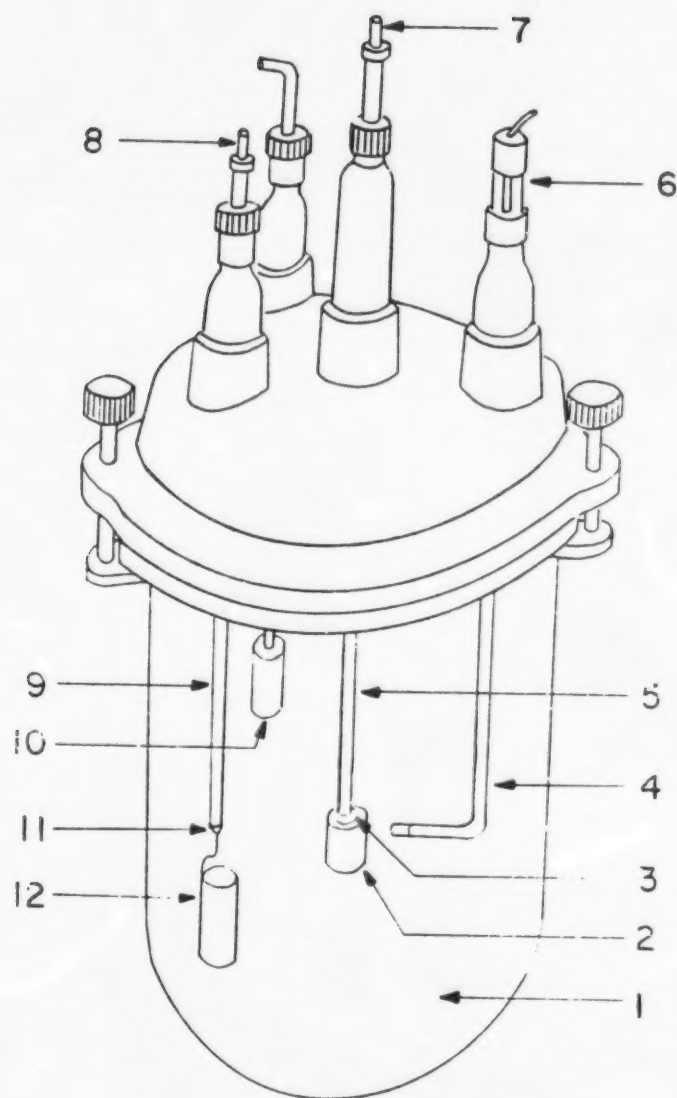


Fig. 3. Schematic diagram of test cell: 1. Reaction kettle; 2. Steel specimen; 3. Epoxy and rubber-o-ring connection; 4. Salt bridge; 5. Glass electrode holder; 6. Reference electrode; 7. Steel rod A (connected to the steel specimen); 8. Steel rod B (connected to the counter electrode); 9. Glass electrode holder; 10. Gas inlet; 11. Epoxy sealing; 12. Counter electrode

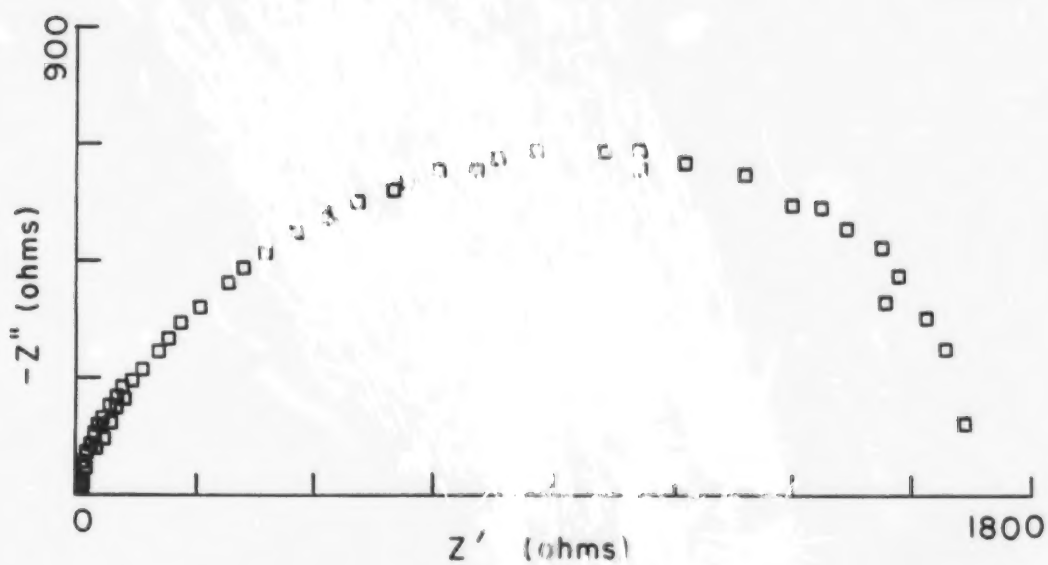


Fig. 4. Nyquist plot 1: Steel sample in oxygenated water containing 1 % calcium chloride

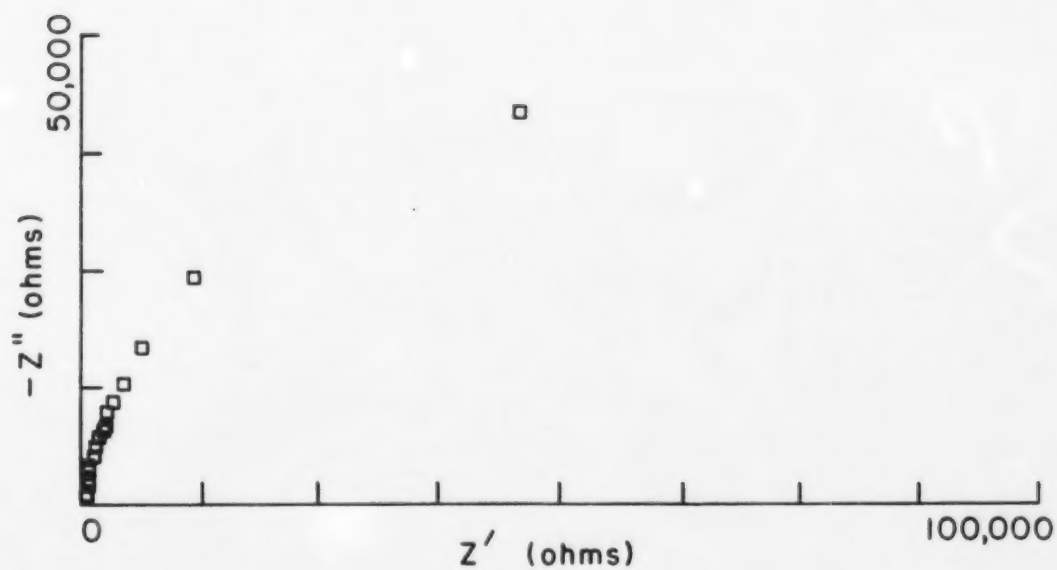


Fig. 5. Nyquist plot 2: Steel sample in oxygenated lime water containing 1 % calcium chloride and 0.1 % calcium nitrite powder

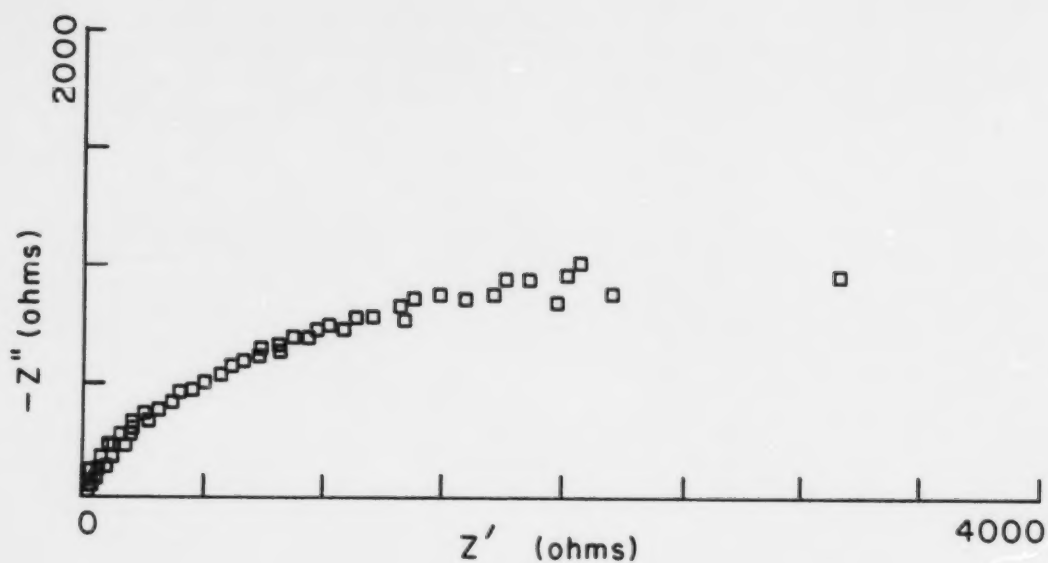


Fig. 6. Nyquist plot 3: Steel sample in oxygenated lime water containing 0.1 % calcium nitrite powder and 2 % calcium chloride

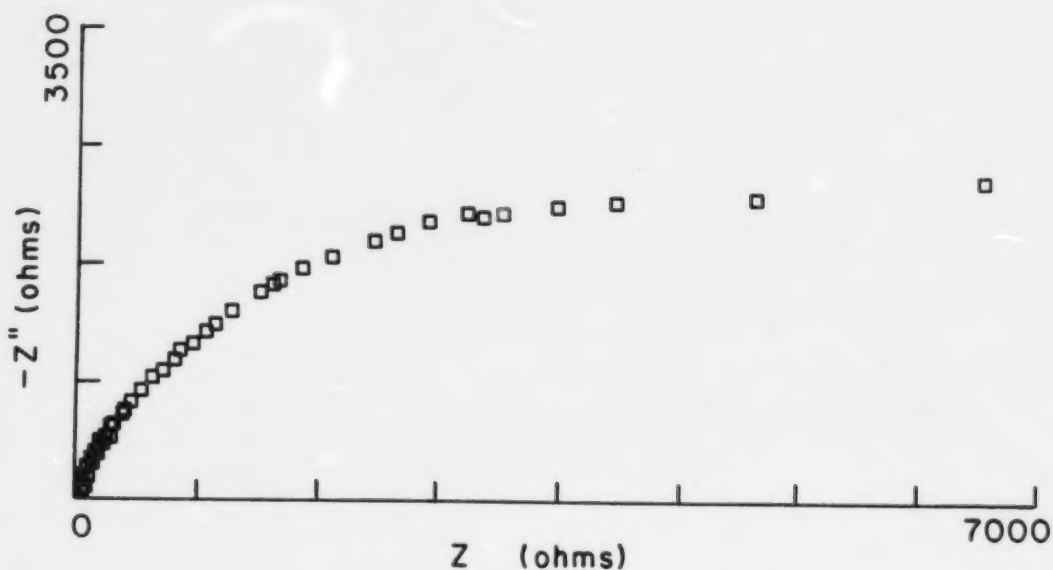


Fig. 7. Nyquist plot 4: Steel sample in 6-month old oxygenated lime water containing 1 % calcium chloride, 0.3 % calcium nitrite powder and 0.1 % iron filings

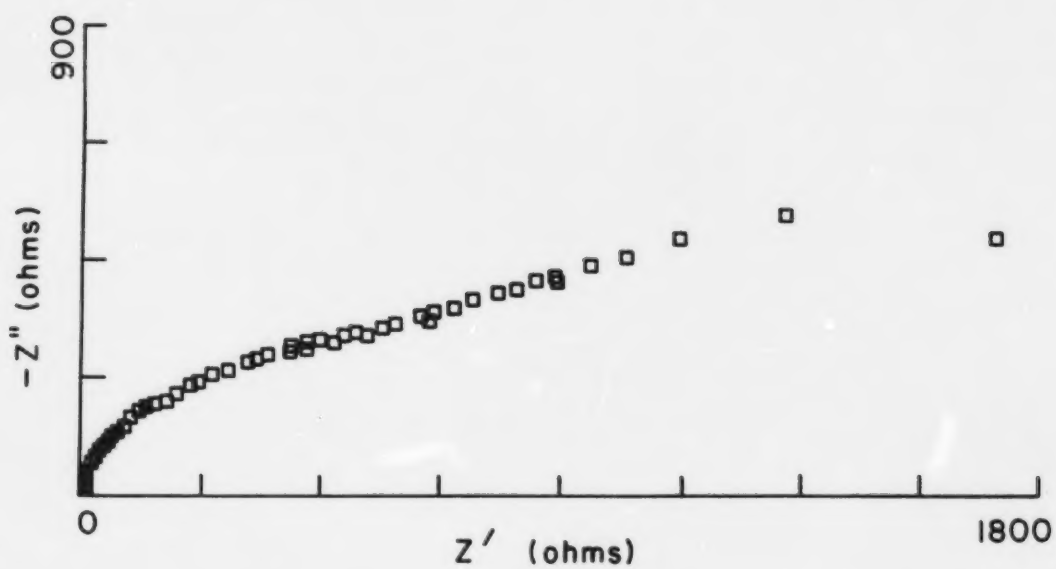


Fig. 8. Nyquist plot 5: Steel sample in oxygenated lime water containing 1 % calcium chloride and 0.1 % stannous chloride

APPENDIX

Recommendation for Phase II Study

The original contract proposal suggested that the investigation be conducted in two parts. Phase I concerned a study of the electrochemistry of commercially available corrosion inhibitors and, as far as calcium nitrite is concerned, the results of this study are promising.

It is recommended that Phase II be a study of the effectiveness of calcium nitrite in actual concrete samples. A recommended study for Phase II is as follows.

Experimental

Concrete specimens containing three embedded rebars will be manufactured containing 0, 0.1, 0.2, 0.3, 0.5, and 1.0 % calcium nitrite by mass of cement. The concrete will be air entrained concrete with a water-cement ratio of 0.50 and nominal 75 mm slump. Nine specimens will be manufactured from each mix. The mix containing 0 % calcium nitrite will be used as the control.

Following 28 days moist curing, three specimens from each batch will be subject to the following regimes.

Three specimens will be alternately saturated for 3 days in 3.5 % sodium chloride solution followed by 11 days drying in laboratory air.

Three specimens will be alternately oven dried for 7 days, saturated in 3.5 % sodium chloride solution for 7 days followed by drying in laboratory air for 28 days.

Three specimens will be stored outdoors and ponded with 3.5 % sodium chloride solution for 7 days followed by air drying for 21 days.

Electrochemical corrosion rate measurements will be performed periodically on all specimens and polarization resistance, AC impedance, half-cell potential, and concrete electrical resistance will be measured.

It is expected that these experiments will continue over an 24-month period during which time it should become apparent if the nitrite inhibitor is being consumed and at what rate.